PAMS Data Validation

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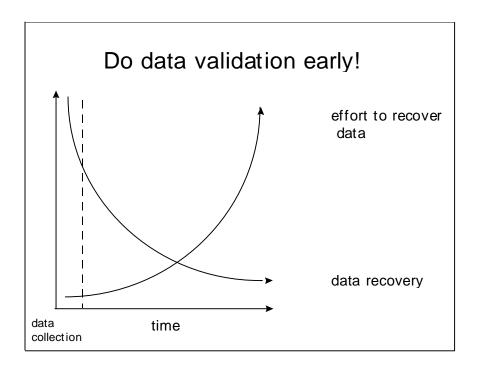
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Introduction

- This section provides example procedures for validating data collected at PAMS sites including routine air quality measurements (e.g., ozone, NO_x), routine meteorological measurements, and VOC measurements.
- Data validation of upper-air meteorological measurements collected as a part of the PAMS network are discussed in a separate section of the workbook.
- Several comprehensive documents exist regarding data quality control and quality assurance of PAMS VOC data (U.S. EPA, 1998), routine air quality and meteorological data, and upper-air meteorological data.
- The intended audience of this section of the workbook is the data analyst who wishes to explore the rich PAMS database.
- The principal topic of this section is VOC data validation with a focus on Level 1-3 validation (i.e., internal, temporal, and spatial consistency).

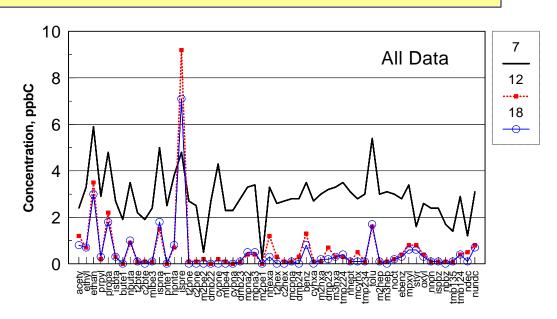
The Importance of Data Validation (1 of 2)

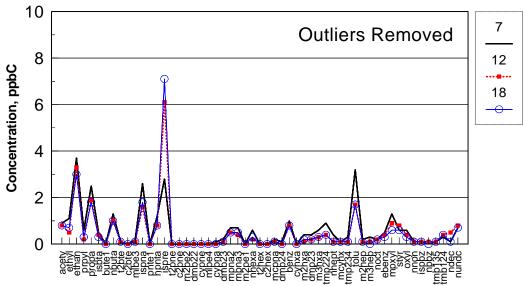
- Data validation is critical because serious errors in data analysis and modeling results can be caused by erroneous individual data values.
- Data validation consists of procedures developed to identify deviations from measurement assumptions and procedures.
- Timely data validation is required to minimize the generation of additional data that may be invalid or suspect and to maximize the recoverable data.



The Importance of Data Validation (2 of 2)

- In this example, data were averaged over the month of July 1995 at a PAMS site for 0700, 1200, and 1800 ST.
- The 0700 data stand out as significantly different from the other two time periods.
- One might expect high concentrations in the morning due to traffic and low mixing heights. However, measurements were at very a rural site.
- Upon further investigation, several high concentration calibration runs remained in the data set at 0700 ST. Once these data were removed, the three time periods are much more similar as expected for the site.
- Without careful screening of data, the wrong conclusions may be drawn.





Data Validation Definitions (1 of 3)

Outliers: Data spatially, temporally, or physically (e.g., reported NO+NO₂ \neq NO_x or ozone concentration > 500 ppb) inconsistent.

Level 0 Data Validation: Routine checks made during the initial data processing and generation of data, including proper data file identification, review of unusual events, review of field data sheets and result reports, instrument performance checks and deterministic relationships.

- Verify computer file entries against data sheets.
- Flag samples when significant deviations from measurement assumptions have occurred.
- Eliminate values for measurements that are known to be invalid because of instrument malfunctions.
- Replace data from a backup data acquisition system in the event of failure of the primary system.
- Adjust measurement values of quantifiable calibration or interference bias.
- Document the changes made to the database.

Data Validation Definitions (2 of 3)

Level I Data Validation: Tests for internal consistency to identify values in the data which appear atypical when compared to values of the entire data set.

- Investigate time series of hydrocarbons (e.g., are expected diurnal patterns evident?).
- Investigate relationships among hydrocarbons using scatter plots.

Level II Data Validation: Comparison of the current data set with historical data to verify consistency over time. This level can be considered a part of the data interpretation or analysis process.

- Investigate abundant species and fingerprints (e.g., what changes have occurred over time?)
- Investigate spatial and temporal characteristics of the data.

Data Validation Definitions (3 of 3)

Level III Data Validation: Tests for parallel consistency with data sets from the same population (i.e., region, period of time, air mass, etc.) to identify systematic bias. This level can also be considered a part of the data interpretation or analysis process.

Compare VOC speciation and concentration among sites using special studies data, etc. How well do the data compare? Are differences explained by meteorology, photochemistry, analytical differences, etc.?
U.S. EPA, 1980

Example data validation notes for a PAMS site indicating the sample date, time, QC code, affected species or sample, number of flagged samples, and comments.

| Date | Time | QC | Species or Sample | Flagged Samples | Comments | |
|---------|-------------|---------|---------------------|--------------------|--|--|
| 8/10/95 | 12:00 | Suspect | i-propylbenzene | 1 | Isolated high concentration | |
| 9/15/95 | 600 | Suspect | i-propylbenzene | 1 | Isolated high concentration | |
| 8/31/95 | 3 & 9-21:00 | Invalid | Sample | 5 | High unidentified; nearly equal to TNMOC | |
| 9/12/95 | 3:00 | Suspect | Sample | 1 | TNMOC missing, negative unidentified | |
| 9/15/95 | 3 & 6:00 | Invalid | unidentified, TNMOC | 2 | 2 TNMOC unit code error? thus unidentified<0 | |
| 9/27/95 | 300 | Suspect | Sample | 1 | Missing propane | |

Data Validation Procedures and Results

- Assemble the Level 0 or Level I database.
- Place data in a common data format with descriptive information concerning variables, validation level, QC codes, time standard, and standard units.
- Ensure that results of and suggestions from final audit reports have been incorporated into the database.
- Review simple statistics for unrealistic maxima or minima and for consistency with nearby stations (data are still Level I).
- Perform spatial and temporal comparisons of the data (begin Level II).
- Perform intercomparisons of the data (e.g., from two different instruments). Data are now Level III.

AIRS Null Data Reason Codes

- Example description of codes used to nullify data in AIRS.
- Knowledge of these codes helps the data analyst understand why data are missing from a database.

| CODE | DESCRIPTION | |
|------|--------------------------------|--|
| 9973 | SAMPLE TIME OUT OF LIMITS | |
| 9974 | SAMPLE FLOW RATE OUT OF LIMITS | |
| 9978 | INVALIDATED BY OPERATOR | |
| 9979 | MISCELLANEOUS VOID | |
| 9980 | MACHINE MALFUNCTION | |
| 9984 | LAB ERROR | |
| 9985 | POOR QUALITY ASSURANCE RESULTS | |
| 9986 | CALIBRATION | |
| 9990 | PRECISION CHECK (PREC) | |
| 9991 | QC CONTROL POINTS (ZERO/SPAN) | |
| 9992 | QC AUDIT (AUDIT) | |
| 9993 | MAINTENANCE/ROUTINE REPAIRS | |
| 9995 | MULTI-POINT CALIBRATION | |
| 9996 | AUTO CALIBRATION | |

U.S.EPA, 1989

Definitions Used In This Workbook

- Sum of PAMS Target Species (PAMSHC, 43000):
 - sum of 55 C_2 - C_{12} identified hydrocarbons
- Total Nonmethane Organic Compounds (TNMOC, 43102):
 - sum of identified hydrocarbons and unidentified mass from C_2 through C_{12} (PAMSHC + unidentified).
- Nonmethane Hydrocarbons (NMHC):
 - Also typically defined as the sum of identified hydrocarbons and unidentified mass.
- Volatile Organic Compounds (VOC):
 - Used in this presentation interchangeably with TNMOC, NMHC.

Definitions of TNMOC, NMHC, and VOC can vary widely because they are operational (i.e., based on the analytical techniques used).

PAMS Target Volatile Organic Compounds

| AIRS No. | Abbreviation | Compound |
|----------|--------------|------------------------|
| 43203 | ethyl | Ethylene |
| 43206 | acety | Acetylene |
| 43202 | ethan | Ethane |
| 43205 | prpyl | Propylene |
| 43204 | propa | Propane |
| 43214 | isbta | Isobutane |
| 43280 | 1bute | 1-Butene |
| 43212 | nbuta | n-Butane |
| 43216 | t2bte | trans-2-Butene |
| 43217 | c2bte | cis-2-Butene |
| 43221 | ispna | Isopentane |
| 43224 | 1pnte | 1-Pentene |
| 43220 | npnta | n-Pentane |
| 43243 | ispre | Isoprene |
| 43226 | t2pne | trans-2-Pentene |
| 43227 | c2pne | cis-2-Pentene |
| 43244 | 22dmb | 2,2-Dimethylbutane |
| 43242 | cypna | Cyclopentane |
| 43284 | 23dmb | 2,3-Dimethylbutane |
| 43285 | 2mpna | 2-Methylpentane |
| 43230 | 3mpna | 3-Methylpentane |
| 43231 | nhexa | n-Hexane |
| 43262 | mcpna | Methylcyclopentane |
| 43247 | 24dmp | 2,4-Dimethylpentane |
| 45201 | benz | Benzene |
| 43248 | cyhxa | Cyclohexane |
| 43263 | 2mhxa | 2-Methylhexane |
| 43291 | 23dmp | 2,3-Dimethylpentane |
| 43249 | 3mhxa | 3-Methylhexane |
| 43250 | 224tmp | 2,2,4-Trimethylpentane |

| AIRS No. | Abbreviation | Compound |
|----------|--------------|------------------------------|
| 43232 | nhept | n-Heptane |
| 43261 | mcyhx | Methylcyclohexane |
| 43252 | 234tmp | 2,3,4-Trimethylpentane |
| 45202 | tolu | Toluene |
| 43960 | 2mhep | 2-Methylheptane |
| 43253 | 3mhep | 3-Methylheptane |
| 43233 | noct | n-Octane |
| 45203 | ebenz | Ethylbenzene |
| 45109 | m/pxy | m/p-Xylene |
| 45220 | styr | Styrene |
| 45204 | oxyl | o-Xylene |
| 43235 | nnon | n-Nonane |
| 45210 | ispbz | Isopropylbenzene |
| 45209 | npbz | n-Propylbenzene |
| 45212 | metol | m-Ethyltoluene |
| 45213 | petol | p-Ethyltoluene |
| 45207 | 135tmb | 1,3,5-Trimethylbenzene |
| 45211 | oetol | o-Ethyltoluene |
| 45208 | 124tmb | 1,2,4-Trimethylbenzene |
| 43238 | ndec | n-Decane |
| 45225 | 123tmb | 1,2,3-Trimethylbenzene |
| 45218 | mdeben | m-Diethylbenzene |
| 45219 | pdeben | p-Diethylbenzene |
| 43954 | nundc | n-Undecane |
| 43502 | form | Formaldehyde |
| 43551 | acet | Acetone (optional) |
| 43503 | aceta | Acetaldehyde |
| 43000 | PAMHC | Sum of PAMS target compounds |
| 43102 | TNMOC | Total NMOC |

Abbreviations from the PAMS manual.

U.S. EPA, 1998 PAMSgram #9, #15

Available Tools and Methods

Tools and methods available to investigate the validity of the PAMS data include the following:

- Statistical software and related tools (e.g., AMDAS from http://www.environ.org/amdas).
- PAMS VOC data validation tool (e.g., VOCDat from ftp://ftp.sonomatech.com/public/vocdat/).
- Spreadsheets and graphical packages

Example VOC Data Validation Tools (1 of 2)

VOCDat software is used to import and display VOC data, perform QC tasks on the data, and begin data analyses.

- Import and export AIRS AMP370 format
- Import Turbochrome auto-GC software format from Perkin-Elmer systems
- Edit data QC codes on screen (keeps a log of changes)
- Prepare graphical displays of time series, scatter, and fingerprint plots
- Perform QC screening checks
- Provides summary statistics
- Customizable species list
- Customizable screening criteria

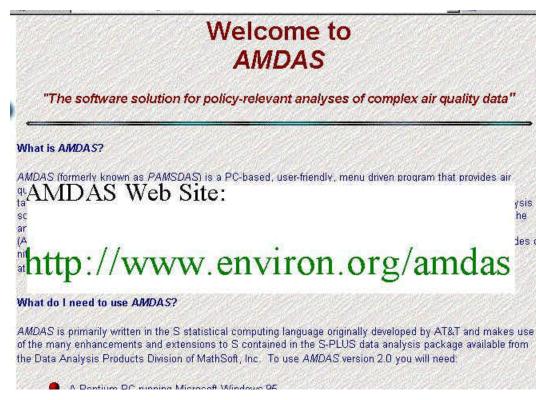
- Calculates species group sums including paraffins, olefins, aromatics, unidentified, carbonyls, and PAMS target species
- Available free at:
 <u>ftp://ftp.sonomatech.com/public/vocdat/</u>
 or through an EPA website link
 <u>http://www.epa.gov/oar/oaqps/pams/analysis.html</u>
- To register for notification of software updates: e-mail *hilary@sonomatech.com*

Main et al., 1998

Example VOC Data Validation Tools (2 of 2)

Plotting capabilities

- Time series
- Scatter plot matrices
- Regression analysis
 (simple, overlaid simple, multiple regression)
- Side-by-side box plots
- Diurnal profiles
- Fingerprint plots
- Pollution rose



Stoeckenius, 1999

AMDAS requires S-Plus for Windows version 4.5 or above

Examples of Problems Encountered in Databases (and Validation Actions) (1 of 2)

- Air quality data reported during calibration runs. For example, ozone data with values of 0 ppb reported when instruments are known to be automatically calibrated. *Data were flagged as "calibration"*.
- Nitrogen oxides data found to have a constant offset based on comparisons of NO_x to NO+NO₂. *Data were adjusted*.
- Data which were physically consistent (i.e., reasonable values) and thus passed statistical checks, but were spatially inconsistent. For example, calm winds observed at a site when all nearby sites measured strong winds; *calm winds were flagged as "suspect"*.
- Ozonesonde surface measurements consistently lower than measurements from a collocated surface monitor. *Concentrations were adjusted for measurement bias*.
- Ground clutter, migrating birds, and precipitation affected radar profiler measurements. *Affected measurements were invalidated*.

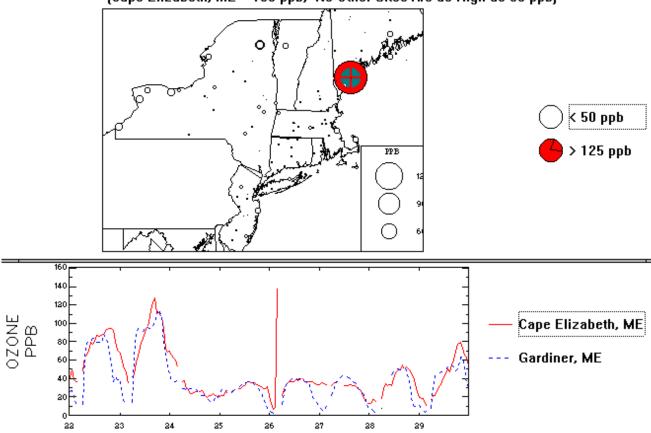
Examples of Problems Encountered in Databases (and Validation Actions) (2 of 2)

- High propane concentrations (i.e., more than two orders of magnitude higher than at other sites) were observed. Site operator discovered leak in a propane tank in the sampler shelter. *Propane concentrations were* "invalidated".
- Cold trap failure on an auto-GC identified with scatter plot of ethane to benzene. *Species below C4, species group totals, and total NMHC were invalidated.*
- Misidentified hydrocarbons were found using scatterplots and time series. Data were flagged as "suspect" and referred back to the reporting agency for correction.
- Other VOC contamination incidences including high concentrations of one hydrocarbon commonly used as a blowing agent with a steady decline over time (identified as shelter off-gassing), high concentrations of several samples with a fingerprint similar to gasoline vapor (identified as spilled fuel from a nearby farmer during refueling). *Data were invalidated upon confirmation of the problem*.

Example Ozone Validation (1 of 3)

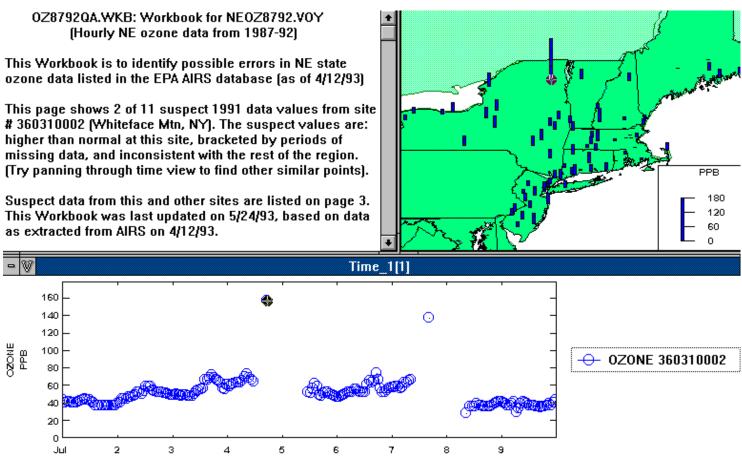
Reported Regional Ozone Concentrations at 4 A.M. on May 26, 1992

(Cape Elizabeth, ME = 139 ppb; No Other Sites Are as High as 50 ppb)



Example of identification of suspect data values from the Northeast (NESCAUM, 1993). The ozone concentration of 139 ppb reported at Cape Elizabeth on May 26, 1992 at 4:00 a.m. appears erroneous when viewed in a spatial and temporal context.

Example Ozone Validation (2 of 3)



Example of identification of suspect data values from the Northeast (NESCAUM, 1993). Two values are anomalously high when inspected both temporally and spatially.

Example Ozone Validation (3 of 3)

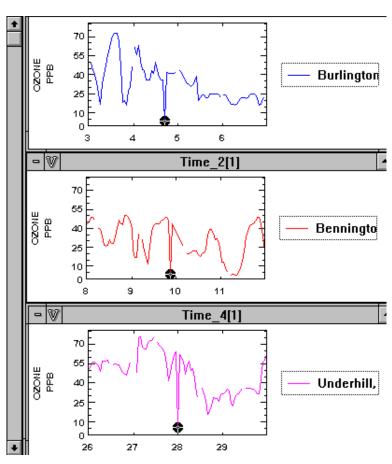
A close look at the hourly data from 3 Vermont sites shows a number of isolated hourly values which are anomolously lower (by at least 20 ppb) than the reported concentrations in the preceeding and following hours.

In nearly every case, these appear to result from a misplaced decimal point. For example:

| Location | Burlington | Bennington | Underhill |
|----------|------------|------------|-----------|
| Date | 9/4/88 | 6/10/90 | 8/28/91 |
| Time | 17:00 | 16:00 | 12:00 |
| # Before | 36 ppb | 47 ppb | 64 ppb |
| # in ? | 4 ppb | 4 ppb | 6 ррь |
| # After | 42 ppb | 44 ppb | 62 ppb |

These "slipped decimal points" may have gone undetected since all are on the low end & consequently unimportant with respect to attainment status.

These and other suspect data values are listed on the following page. Other suspect data values will be added to this workbook as they are identified.

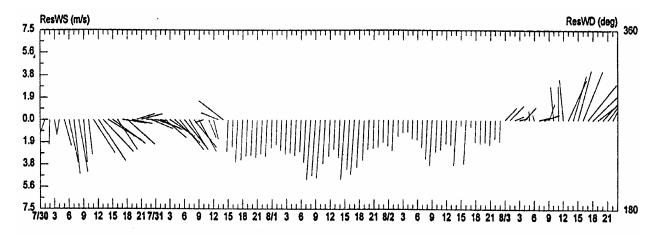


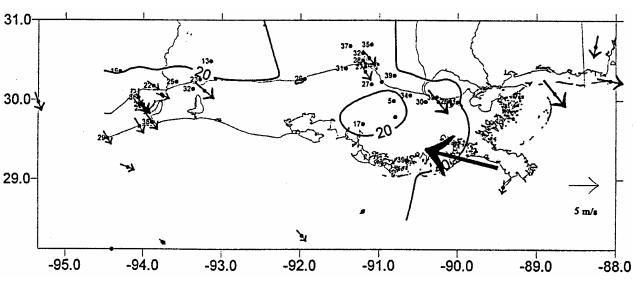
Example of identification of suspect data values from the Northeast (NESCAUM, 1993). Reported isolated low values were probably the result of misplaced decimal points.

Example Meteorological Data Validation

Examples of questionable meteorological data identified during data validation (SAI et al., 1995).

- At top, constant wind directions were reported at Cocodrie, Louisiana from July 31 August 2, 1993. The wind direction data were invalidated.
- At bottom, high surface winds at a surface station in Grand Isle, Louisiana on August 29, 1993 at 0800 CST appear spatially erroneous.





VOC Data Validation Tasks (1 of 2)

- Assess audit results (accuracy).
- Assess laboratory and field blank results.
- Assess collocated sample results (overall precision) and replicate analyses (analytical precision).
- Compare reported speciation to other databases. *Have all the important species been measured?*
- Prepare univariate statistics of concentration and weight fraction:
 - Stratify by date, time of day, and sampling location.
 - Determine completeness of data.

VOC Data Validation Tasks (2 of 2)

- Use graphical procedures including scatter, box-whisker, time series, and fingerprint plots.
- Perform internal consistency checks using ratios of individual species or species group concentrations to other species, TNMOC, and CO.
- Example guidelines for flagging samples for further inspection:
 - Species exceeds 20 percent of the TNMOC or is 3 sigma above the mean of that species.
 - Total unidentified TNMOC exceeds 15 percent (or user-defined) or is negative (i.e., reported total TNMOC is less than the sum of identified species).
 - Normally abundant species present in low concentrations when concentrations of other species are high.

Tips and Tricks for VOC QC and Data Analysis (1 of 3)

Overall

- Proceed from the big picture to the details. For example, proceed from inspecting total VOC to species groups to individual species.
- Inspect every species, even to confirm that a species normally absent met that expectation.
- Know the site topography, prevalent meteorology, and major emissions sources nearby.

• Inspect time series for the following:

- Large "jumps" or "dips" in the concentrations
- Periodicity of peaks
- Evidence of calibration gas carryover into hours following a calibration
- Expected diurnal behavior (i.e., biogenic isoprene concentrations usually peak during midday or late afternoon)
- Expected relationships among species
- High single-hour concentrations of less abundant species

Tips and Tricks for VOC QC and Data Analysis (2 of 3)

- Prepare scatter plots of the following:
 - Total NMOC vs. species groups (i.e., aromatics, paraffins)
 - Total NMOC vs. all individual species
 - Benzene vs. acetylene and toluene (these species typically correlate, with some toluene outliers where toluene is greater than benzene)
 - Benzene vs. cyclohexane (look for split in the scatter plot indicating misidentification)
 - Benzene vs. ethane (low or missing ethane concentrations when benzene is abundant may indicate cold trap problems)
 - Species that elute close together, e.g., 2,3-dimethylbutane,
 2-methylpentane, and 3-methylpentane
 - Isomers (e.g., o-, m-, and p-xylene)

Tips and Tricks for VOC QC and Data Analysis (3 of 3)

- Prepare and inspect fingerprint plots for the following:
 - Identify calibration data.
 - Investigate hours surrounding suspect and invalid data.
 - Obtain overall view of diurnal changes.
- To further investigate outliers:
 - Use wind direction data (e.g., do outliers occur from a consistent wind direction?)
 - Use other criteria pollutant data (e.g., ozone, NO_x)
 - Use subsets of data (e.g., inspect high ozone days vs. other days)
 - Investigate industrial or agricultural operating schedules, unusual event occurrence, etc.
 - Determine local traffic patterns (e.g., when does peak traffic occur?)

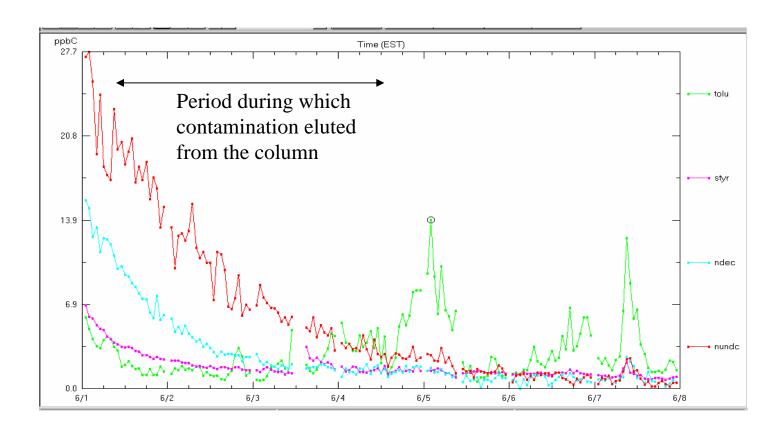
Example Screening Criteria

- Check that abundant hydrocarbons (e.g., acetylene, ethane, propane, n-butane, i-pentane, n-pentane, n-hexane, benzene, toluene, m-&p-xylenes) are present in the same samples. This check helps identify "missing" abundant hydrocarbons. Set the screening concentrations sufficiently higher than the detection limit (e.g., 10 times) to limit the number of data "failing" these criteria.
- Check that the data meet expected relationships. For example, n-pentane concentrations are usually less than i-pentane concentrations. Other possible screens include o-xylene < m-&p-xylenes and benzene < toluene.
- Check for unusual sample compositions including
 - ethane concentration < 2 ppbC but benzene > 2 ppbC (may indicate cold trap problems)
 - unidentified fraction of TNMOC > 50% (the less known about a sample's composition, the less useful the sample).

These checks should be used as a starting point for data validation and not as hard and fast rules; there are always exceptions!

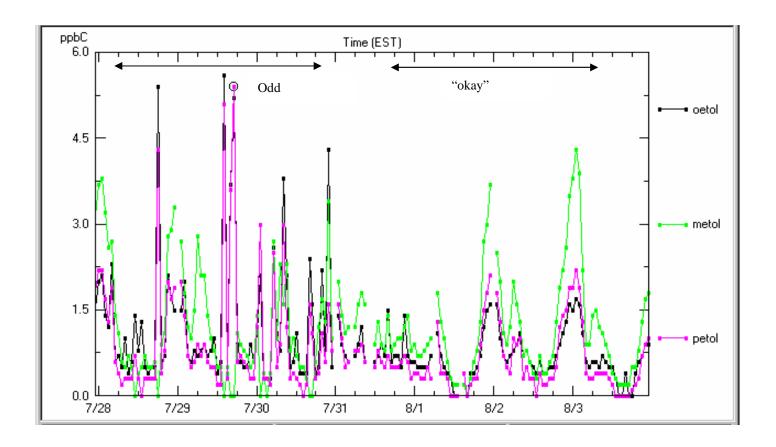
Main et al., 1998

Example of Start-up Problems



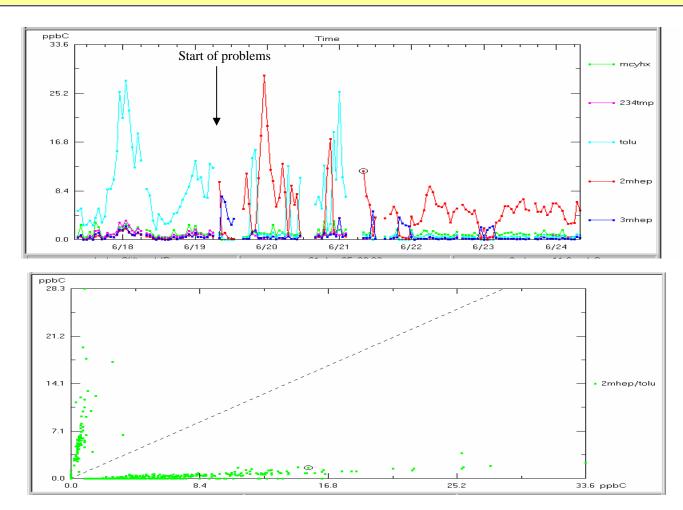
Time series plots of species groups (top) and individual species (bottom) at a PAMS site during early June 1996. Example of possible contamination of either the shelter air or the analytical equipment. (Level 1, AIRS data) Data during this time period were invalidated.

Example of Odd Data



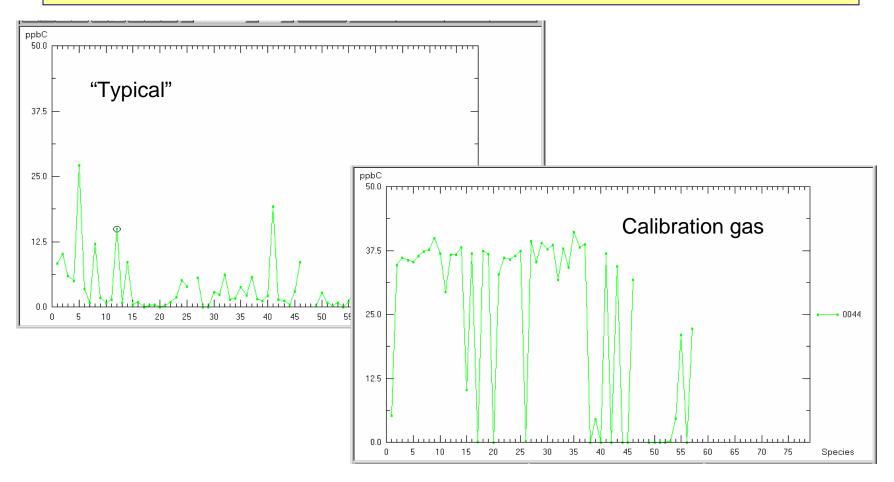
Example of an analytical system change between two months that affected the relationship between three isomers. The p- and o-ethyltoluene concentrations were typically high together when m-ethyltoluene concentrations were reported as 0 ppbC (possible misidentification?) during July. In August, this occurrence was not noted (Main et al., 1999). These data were reinvestigated by the reporting agency.

Example of Peak Misidentification



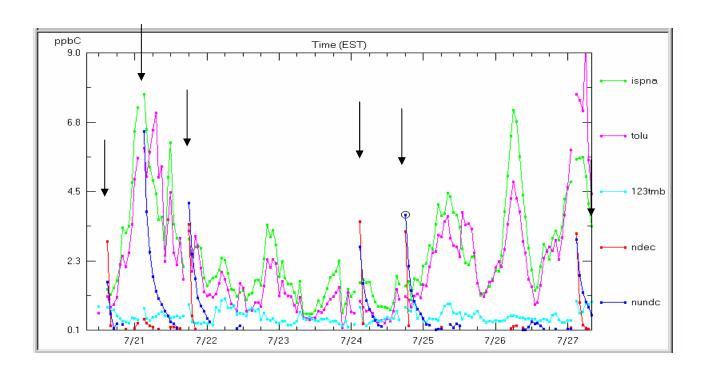
Example of finding species misidentification in a data set using a time series plot (top) and scatter plot (bottom). In this example, 2-methylheptane and 3-methylheptane peaks were misidentified as toluene beginning on June 19. Data were collected at a PAMS site during June 1995. (Level 0, AIRS) Typical scatter plots may show well-defined edges but will have data values filling in the area between the edges. These data were corrected by the reporting agency.

Example of Calibration Gas Fingerprint



Examples of typical (top) and calibration (bottom) fingerprints. Hydrocarbon species are listed in order of elution from the gas chromatograph and in these plots are represented by numbers. Typical fingerprints show low concentration of many of the hydrocarbons and higher concentrations of others. The calibration gases typically contain roughly the same concentration of each hydrocarbon (e.g., about 35 ppbC) with a few species missing from the mixture. (Level 1, AIRS data) Calibration data need to be identified as such and not used in any analyses of the ambient data.

Example Calibration Gas Carryover



Example of possible calibration carryover in data collected at a PAMS site during July 1995. Note relatively high concentrations of n-undecane, for example, occurring after an hour with missing data and the "tailing off" of concentrations over the next few hours. (Level 0, AIRS) Typically, only a few species are affected by carryover, and these species should be invalidated in the affected samples.

Data Access (1 of 2)

Official data sources:

- AIRS Data via public web at http://www.epa.gov/airsdata
- AIRS Air Quality System (AQS) via registered users register with EPA/NCC (703-487-4630)

Other key PAMS data analysis sources:

- Ambient Monitoring Technology Information Center (AMTIC)
 at http://www.epa.gov/ttn/amtic/pamsmain.html
- PAMS Data Analysis clearinghouse at

http://www.epa.gov/oar/oaqps/pams and

http://capita.wustl.edu/EnhancedOzone.

Data Access (2 of 2)

Secondary data sources:

- Meteorological parameters from National Weather Service
 (NWS) http://www.nws.noaa.gov
- Meteorological parameters from PAMS/AIRS AQS register with EPA/NCC (703-487-4630)
- Collocated or nearby SO₂, nitrogen oxides, CO, VOC from AIRS AQS
- Private meteorological agencies (e.g., forestry service, agricultural monitoring, industrial facilities)

Summary

- Data validation is vital because serious errors in data analysis and modeling results can be caused by erroneous individual data values.
- Once initial data validation steps have been taken, data validation continues throughout the data interpretation process.
- Overall data validation guidelines include:
 - Proceed from the big picture to the details.
 - Inspect every species, even to confirm that a species normally absent met that expectation.
 - Know the site topography, prevalent meteorology, and major emissions sources nearby.
- This workbook section provides a discussion of data validation levels, example validation checks, available data validation tools, and suggested steps to take in the data validation process.

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